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RESEARCH ON THERMAL TRANSFER PHENOMENA  
Third Quarterly Status Report  
for the Period July 1 through Sept. 30, 1965  
Contract NASw-1197  
NATIONAL BERYLLIA CORPORATION  
Haskell, New Jersey

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# ABSTRACT

12/68  
Magnesia-stabilized zirconia foams have been produced, which have a fired strength of 700 to 800 psi, an eightfold increase over the best strength previously obtained. As a result of this improvement, it has been possible to obtain thermal conductivity data to 2500°C (4532°F); a temperature approaching the melting point of this composition. The radiation component of heat transfer at temperatures above 3000°F seems to be almost as effectively minimized by scattering from the particle and pore surfaces themselves as by metallic or barrier phase additives.

Program for the final quarter will include optimization of density and strength, further work on metallic reflectors, and improvements in precision of thermal conductivity data.

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## 1. INTRODUCTION

This is the Third Quarterly Report on Contract NASw-1197, entitled "Research on Thermal Transfer Phenomena." This program is a continuation of work performed on Contract NASr-99 (April, 1962-December, 1963) and Contract NASw-884 (January-December, 1964), both entitled "Research on Low Density Thermal Insulation Materials for Use Above 3000°F."

### 1.1 Purpose of the Program

Low density ceraric insulation materials have long been considered to lose efficiency as thermal insulators, above 2400°F, because of heat transfer through the pores by radiation. An object of this program has been to study the reduction of this radiation (photon) contribution to thermal conductivity by incorporating a radiation barrier phase into a porous structure. Mechanisms which were to be investigated include absorption and re-radiation by embedded particles, scattering by incorporated phases, and reflection by metallic film radiation barriers.

### 1.2 Summary of Previous Work

Under Contract NASr-99, lightweight porous bodies were developed from several pure refractory oxides, including  $ZrO_2$  and  $MgO$ , and physical property data compiled. Equipment was designed and built to measure thermal conductivity to temperatures in the range 2500°C (4500°F). Development work has been

concentrated on calcia-stabilized  $ZrO_2$  foam structures. The properties of bodies containing dispersed radiation barriers such as carbonaceous material and metallic inclusions were compared with those of the basic matrix composition.

Property limitations of oxide raw materials intended for use above 4000°F were met and overcome. Attenuation of the thermal radiation component by carbon-base phases was shown to be limited. However, the incorporation of refractory metal reflecting phases within the ceramic matrix appeared promising.

Under Contract NASw-884, this latter improvement in heat transfer by metallic phases was confirmed, the placement and dispersion of the radiation barrier having a critical influence. The validity of the thermal conductivity data was confirmed by comparative testing at other laboratories. Further material limitations in the upper temperature range were encountered, and effort was directed toward the improvement of structural stability of the ceramic foam matrix at high temperatures.

### 1.3 Program Tasks

The objectives of the present contract comprise the following two tasks:

Task A - Research on Composite Insulation Leading to  
Increased Reliability in Thermal Measurements

Four approaches were outlined as possible means of improving

the strength of the calcia-stabilized  $ZrO_2$  foam structures: reinforcement with stabilized zirconia fibers; incorporation of metallic zirconium; maximization of particle contact by control of particle size distribution; and development of metallic coatings and strengtheners. Experiments with the first two approaches show no significant effect, but the latter two approaches appear promising.

#### Task B - Finalization of Static Comparative Measurements

Composites prepared according to one or two of the most promising approaches outlined above are to be measured for thermal conductivity up to 4500°F.

## 2. LITERATURE REVIEW

A new reference <sup>(1)</sup> has just come to hand, which is pertinent to this contract. The author states that "at temperatures above 1800°C, hot BeO exhibited no tendency toward a rapid transfer of radiant energy under the experimental conditions," and "the actual effects produced in the granular BeO material were considered to result from radiant energy emitted by the BeO tube,

- (1) E. J. Chapin and D. G. Howe: An exploratory Study of Radiant Energy Transport in BeO; NRL Report 6195, U. S. Naval Research Laboratory, Washington, D. C.; March 22 1965.



heating the granular material by a process of absorption, re-radiation, and conduction at contact points." His conclusion that BeO becomes more opaque at increasingly high temperatures is suspect because metallic tungsten was observed to deposit onto the beryllia from the heater.

### 3. RESULTS AND DISCUSSION

#### 3.1 Binder Experiments

An attempt was first made to evaluate the effects of the organic constituents used in the Zr36 zirconia foam composition, and to optimize the amounts needed. The data are listed in Table I, with amounts given as per 100 grams  $ZrO_2$ . Moisture loss figures are from the air-set to the oven-dried state. It was found that polyvinyl alcohol causes moisture to be retained within the structure at room temperature, whereas dextrin aids room temperature drying.

On the basis of pore size, Nos. 3, 7, 8 and 9 appear the best. On the basis of fired density, Nos. 2, 3, 4, 5 and 9 appear the best. On the basis of strength, Nos. 1, 3, 9 and 10 appear the best. Nos. 3 and 9 appear favorably in all three tests. No. 9 corresponds to the original binder formulation used in all previous tests with Zr36, but from No. 3 it appears that PVA could be eliminated with no ill effect.

Table I

EXPERIMENTS TO OPTIMIZE ORGANIC BINDER CONTENT

|  |             |             |            |             |             |             |            |            |            |             |
|--|-------------|-------------|------------|-------------|-------------|-------------|------------|------------|------------|-------------|
| Code 34-1-                                 | 1           | 2           | 3          | 4           | 5           | 6           | 7          | 8          | 9          | 10          |
| Dextrin, g                                 | 0           | 1           | 2          | 4           | 0           | 0           | 0          | 1          | 2          | 4           |
| PVA, cc                                    | 0           | 0           | 0          | 0           | 1           | 2           | 4          | 1          | 2          | 4           |
| Green Density, g/cc<br>(dried 4 hrs. 70°C) | 0.30        | 0.27        | 0.28       | 0.27        | 0.30        | 0.36        | 0.45       | 0.37       | 0.34       | 0.27        |
| Moisture Loss, %                           | 37          | 23          | 30         | 31          | 31          | 41          | 46         | 40         | 43         | 39          |
| Pore Size Range,<br>Microns                | 1400<br>300 | 1400<br>400 | 800<br>200 | 1000<br>600 | 1500<br>500 | 1700<br>800 | 800<br>400 | 400<br>100 | 800<br>100 | 1100<br>160 |
| Fired Density, g/cc<br>(1500°C, 4 hrs.)    | 0.79        | 0.63        | 0.60       | 0.62        | 0.64        | 0.69        | 0.71       | 0.71       | 0.66       | 0.68        |
| Modulus of Rupture<br>PSI (average)        | 99          | 62          | 95         | 70          | 74          | 73          | 70         | 72         | 100        | 95          |

### 3.2 Strength Measurement and Variability

Another series of tests was run to compare various means of measuring the strength of the fired foams (Table II). Modulus of rupture of foam No. 34-1-9 was determined using three methods of loading; the averages of all three sets are practically identical. In comparing modulus of rupture with compressive strength (foam No. 16-271-1), the averages were almost the same, but individual compressive strength readings were much less variable than individual moduli. This suggests that a more meaningful average strength can be obtained from a few compressive strength values than from modulus of rupture data. Future strength data will be obtained by this method.

Table II

#### COMPARATIVE STRENGTH TEST MEASUREMENTS

| Code #                                       | <u>16-271-1</u>  | <u>34-1-9</u>   |
|--|--|---|
| Compressive Strength<br>(PSI)                | $\left. \begin{array}{l} 72 \\ 78 \\ 73 \\ 77 \end{array} \right\} \begin{array}{l} 75 \\ \text{Avg.} \end{array}$ |   |
| Modulus of Rupture<br>Water Loading<br>(PSI) |  | $\left. \begin{array}{l} 94 \\ 91 \\ 112 \end{array} \right\} \begin{array}{l} 99 \\ \text{Avg.} \end{array}$   |
| W Shot Loading<br>(PSI)                      | $\left. \begin{array}{l} 43 \\ 63 \\ 61 \\ 81 \end{array} \right\} \begin{array}{l} 62 \\ \text{Avg.} \end{array}$ | $\left. \begin{array}{l} 91 \\ 103 \\ 107 \end{array} \right\} \begin{array}{l} 100 \\ \text{Avg.} \end{array}$ |
| RPC Tester<br>(PSI)                          |  | $\left. \begin{array}{l} 91 \\ 96 \\ 125 \end{array} \right\} \begin{array}{l} 104 \\ \text{Avg.} \end{array}$  |

### 3.3 Colloidal Silica Bonding Experiments

Attempts to form an air-setting bond in zirconia foam with colloidal silica are listed in Table III. Although no real success has been achieved, this method still holds promise with further work on the proper parameters. Ammonium bicarbonate was tried because both ammonia and  $\text{CO}_2$  are setting agents for these silica bonds. The disadvantage of this bond lies in the introduction of silica, which forms a liquid phase at  $1775^\circ\text{C}$  with zirconia. Hence, this system has not been investigated further at this time.

Table III

#### COLLOIDAL SILICA BONDING EXPERIMENTS

| Code #                        | <u>34-4-1</u>   | <u>34-4-2</u>   | <u>34-10-1</u> | <u>34-10-2</u> | <u>34-11-1</u> |
|-------------------------------|-----------------|-----------------|----------------|----------------|----------------|
| Ethyl Silicate, % (#)         | 3.5             | 7.0             |                |                |                |
| pH                            | 5-6             | 5-6             |                |                |                |
| Silica Sol, % (*)             |                 |                 | 3.5            | 3.5            | 3.5            |
| $\text{NH}_4\text{HCO}_3$ , % |                 |                 | 2              | 2              | 4              |
| (as wt.% $\text{SiO}_2$ )     | 1.0             | 2.0             | 1.0            | 1.0            | 1.0            |
| Dried Strength                | Very<br>fragile | Very<br>fragile |                |                |                |
| Green Density                 |                 |                 | 0.86           | 1.2            | 1.0            |
| Fired Density                 | Collapsed       |                 | Collapsed      |                |                |

(#) Tetraethyl Orthosilicate: Matheson, Coleman & Bell, No. TX-275

(\*) Syton brand: Monsanto Chemical Co., No. P-50

### 3.4 Magnesia-Stabilized Zirconia Foams

Since the general levels of strength, density and thermal conductivity of zirconia foams stabilized by calcium oxide have been thoroughly explored in this program with little prospect of major improvement, it was necessary to study other bond systems which would also stabilize the zirconia. Calcia had been added as plaster of Paris (calcium sulfate hemihydrate), forming a hydraulic bond which made the foam rigid within a short time, and then decomposing during firing to yield CaO which forms a solid solution with zirconia. The hardening is so rapid, however, that proper mixing times for the formation of a fine, rather than coarse, bubble structure could not be attained.

Other oxides, such as MgO and  $Y_2O_3$ , also stabilize zirconia in the cubic form so that it does not undergo a crystallographic transformation during heating or cooling. Since MgO forms complex oxychloride and oxysulfate cements in combination with  $MgCl_2$  or  $MgSO_4$  (the former being the so-called "Sorel cements"), this suggested a promising means of achieving a foam structure which would not set as rapidly as the plaster, and which would form a magnesia-stabilized zirconia phase.

Initial experiments (Table IV) showed that density and strength levels comparable to those of the lime-stabilized foams could easily

be produced with MgO and  $\text{MgCl}_2$ . Some experimentation to determine proper ratio of MgO to  $\text{MgCl}_2$  and the best type of MgO, were then undertaken (Table V). United Mineral and Chemical Corp. MgO (No. 6) was selected for trials because it hardened reasonably slowly, and because of its high purity.

Table IV

MAGNESIUM OXYCHLORIDE BONDING EXPERIMENTS

| <u>Code #</u>                                | <u>34-4-3</u> | <u>34-4-4</u> | <u>34-4-5</u> | <u>34-4-6</u> |
|--|---------------|---------------|---------------|---------------|
| Mol Ratio $\frac{\text{MgO}}{\text{MgCl}_2}$ | 2.35          | 4.6           | 2.35          | 4.6           |
| % Equivalent MgO                             | 2.1           | 2.4           | 4.3           | 4.8           |
| Density, G/cc                                |               |               |               |               |
| Air-dried                                    | 0.30          | 0.30          | 0.30          | 0.30          |
| Oven-dried                                   | 0.28          | 0.28          | 0.27          | 0.26          |
| Fired 1550°C                                 | 0.87          | 0.77          | Distorted     | Distorted     |
| Modulus of Rupture                           | 76            | 100           |               |               |
| PSI  |               |               |               |               |
| Fired 1550°C (avg.)                          |               |               |               |               |

Note: Zirconia-base composition  
MgO: Whittaker, Clark and Daniels, #310, Heavy, U.S.P.

Other sources of MgO might work just as well. For every gram of MgO powder, 1 cc of 1.23 density  $\text{MgCl}_2$  solution (26%  $\text{MgCl}_2$ ) was added to the batch.

The results are listed in Table VI. Foaming action was excellent, and mixing could be continued as long as necessary

Table V

MAGNESIUM OXYCHLORIDE SETTING TIMES

| <u>Source of MgO</u><br><u>(see Note)</u>                              | <u>Mol Ratio</u><br><u>MgO/MgCl<sub>2</sub></u> | <u>Hardening Time</u>                      |
|--|---|--|
| 1. Fisher, electronic grade, boiled in water 18 hrs. to form hydioxide | 5.1   | Plastic after 24 hrs.                      |
| 2. Mg. Nitrate, MCB #CB488   | 1.15  | Liquid after 24 hrs.                       |
| 3. WCD, #H222  | 7.4   | Hardened 24 hrs., but liquid layer on top. |
| 4. WCD, #1323  | 7.4   | Hardened 24 hrs., initially tacky.         |
| 5. WCD, USP Heavy  | 7.4   | Same as 4.                                 |
| 6. UMC, 99.96% pure  | 7.4   | Same as 4.                                 |
| 7. Fisher, electronic grade, #M-300                                    | 3.7   | Hardened 24 hrs.                           |
| 8. Mallinckrodt, fired 1000°C  | 6.3   | Hardened 4-5 hrs.                          |
| 9. Mallinckrodt, as rec'd  | 6.3   | Hardened 18 hrs.                           |
| 10. Fisher, electronic grade, fired 850°C                              | 2.0   | Dried 4-5 hrs.                             |

Note: MCB = Matheson, Coleman and Bell  
WCD = Whittaker, Clark and Daniels, Inc.  
UMC = United Mineral and Chemical Corp.

Table VI

MAGNESIUM OXYCHLORIDE FOAMS

| Code #                                       | <u>34-13-1</u> | <u>34-13-2</u> | <u>34-14-1</u> | <u>34-16-1</u> | <u>34-16-2</u> |
|--|----------------|----------------|----------------|----------------|----------------|
| Dextrin, wt. %                               | 0              | 1.0            | 1.0            | 0              | 1.0            |
| Mol ratio $\frac{\text{MgO}}{\text{MgCl}_2}$ | 7.4            | 7.4            | 7.4            | 7.4            | 7.4            |
| % Equivalent MgO                             | 3.4            | 3.4            | 3.4            | 3.4            | 2.3            |
| Max. pore size, mm.                          | 1.0            | 0.4            | 0.7            | 0.5            | 0.5            |
| % Drying loss, 24 hr.<br>@85°C               | 4.0            | 2.0            | 1.7            | 22.8           | 21.9           |
| Density, g/cc,<br>as fired 1550°C            | 0.92           | 1.07           |                | 1.40           | 0.96           |
| Modulus of rupture<br>PSI (fired) avg.       | 437            | 350            | (weak)         | 823            | 719            |

Basic formulation consists of  $\text{ZrO}_2$  powder (lot4), water, and foaming agent. Percent additives above based on 100%  $\text{ZrO}_2$ .

Only 2/3 amount of water used in 34-14-1. MgO was UMC, 99.96% pure.



to eliminate large bubbles. Dextrin was added to some batches as an aid in retaining maximum foam volume during the initial stages of hardening. In mix No. 34-14-1, only 67 cc. of water was added for 100 g. of  $ZrO_2$ , resulting in a thick batter and a very weak fired structure. In the other mixes, however, using a ratio of 100 cc. water to 100 g.  $ZrO_2$ , the strength was much improved, by factors of 4 to 12 over the plaster-bonded foams. Density of the foams is perhaps not as low as could be desired, (0.60-0.70 g/cc), but further attempts will be made to improve this.

A single foam has so far been made using the oxysulfate bond (Table VII), with equally promising results.

Table VII

MAGNESIUM OXYSULFATE FOAM

|  |                |
|--|----------------|
| Code #                                   | <u>34-18-1</u> |
| Dextrin, %                               | 1.0            |
| Mol Ratio $\frac{MgO}{MgSO_4}$           | 10.4           |
| % Equivalent MgO                         | 3.3            |
| Max. pore size, mm.                      | 0.5            |
| Density, as fired,<br>1550°C, g/cc       | 0.86           |
| Modulus of rupture,<br>PSI, avg. (fired) | 376            |

Basic formulation same as in Table VI.

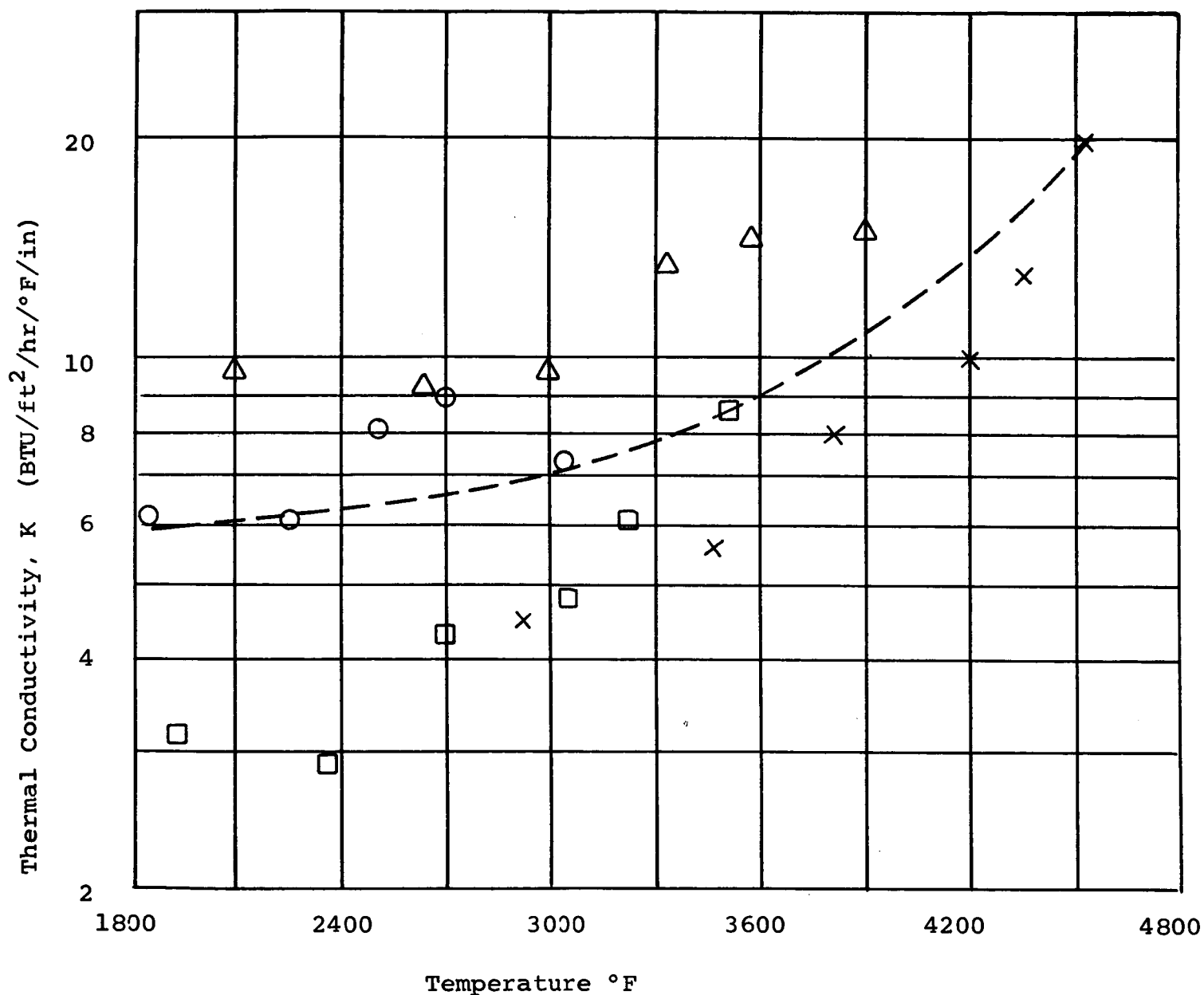
### 3.5 Thermal Conductivity Measurements

The attainment of modulus of rupture values greater than 700 psi for the first time has enabled us to measure thermal conductivity values to higher temperatures than ever before, without failure of the specimen at the sight holes. The curves for the two oxychloride-bonded zirconia foams with highest strength are shown in Figures 1 and 2. In run No. 90, a maximum temperature of 2500°C (4532°F) was reached, closely approaching the melting point of stabilized zirconia. Run No. 91 was terminated at 4000°F only because of heater failure.

Both curves are quite similar at the high end, although at lower temperatures the lower-density material apparently shows slightly lower average K values. The range of conductivity is essentially the same as shown in runs Nos. 86 and 87, Figure 1, in the previous report.

It seems increasingly apparent that the radiation component of heat transfer does not increase nearly as much at high temperatures as predicted, and may not turn out to be a serious obstacle to efficient thermal insulation, using foamed ceramic materials above 3000°F. The grain boundaries between oxide particles or crystallites, as well as the inner surfaces of the pores themselves, may serve well enough as scattering and reflecting surfaces to

FIGURE 1

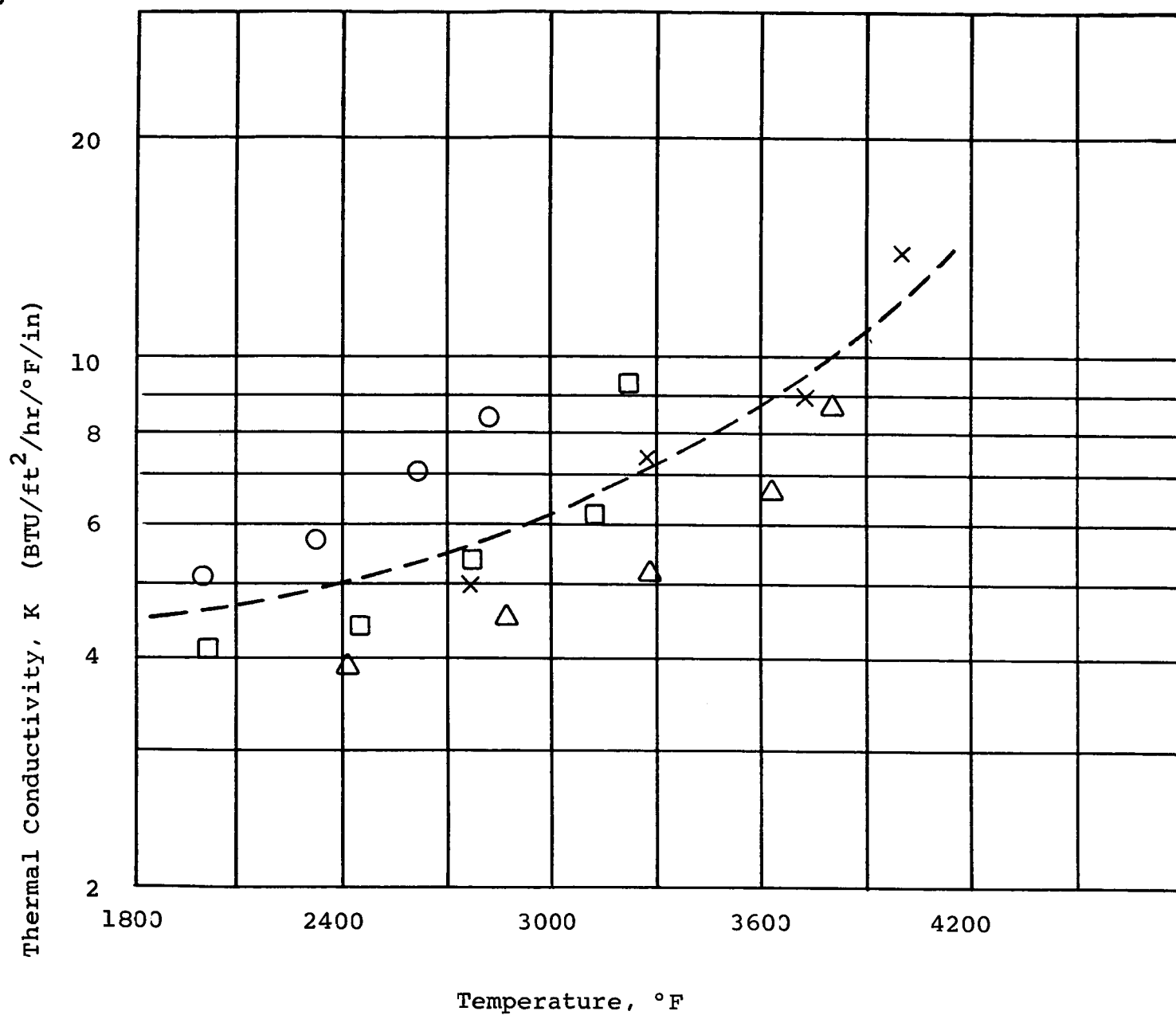


HEAT TRANSFER OF ZIRCONIA FOAM

Run 90: Magnesium Oxychloride Bond (34-16-1)  
(Density: 1.40 g/cc)

|         |   |       |         |   |                              |
|---------|---|-------|---------|---|------------------------------|
| Symbols | X | Gauge | Section | 1 | Adjacent to hot face         |
|         | △ | "     | "       | 2 | 1/8 to 1/4 in. from hot face |
|         | □ | "     | "       | 3 | 1/4 to 3/8 " " " "           |
|         | ○ | "     | "       | 4 | 3/8 to 1/2 " " " "           |

FIGURE 2



#### HEAT TRANSFER OF ZIRCONIA FOAM

Run 91: Magnesium Oxychloride Bond (34-16-2)  
(Density 0.96 g/cc)

Symbols: Same as for Figure 1

render radiant heat transfer across the pore spaces much less important than was previously thought. Metallic reflectors and scattering phases apparently still have a beneficial effect, but the magnitude of this improvement needs to be resolved by more precise thermal conductivity measurements.

#### 4. PROGRAM FOR NEXT QUARTER

The problem of providing sufficient strength to the fired foam (Task A) appears to have been solved by the successful development of magnesium-base cement bonds. Strength has been improved by factors of 4 to 12 times.

Work will be concentrated on diminishing the bulk density of these foams, hopefully, to 0.70 g/cc or less, without significantly sacrificing strength. Variables such as bond concentration, MgO/salt ratio, rate of hardening, amount of foaming agent, and mixing time will be studied.

Since metallic coatings on the foam composite seemed to lower the overall heat transfer value, more work will be done on this line. Bodies prepared from hollow zirconia spheres bonded by a stabilized zirconia matrix will also be evaluated.

The spread in individual conductivity values (Figures 1 and 2) deviates more from the average curve than is desirable.

With a re-evaluation of the method of measurement, and by comparison of values obtained with new equipment of similar design which is now under construction, it is hoped that more reliable static measurements can be submitted in the next report in satisfaction of Task B of this contract.